Morphology and Crystallography of $\beta'$ Martensite in TiNi Alloys

By Shant P. Gupta* and A. A. Johnson*

Martensitic transformation in TiNi alloys of the near-equiatomic composition has been studied by utilizing electron microscopy and diffraction under various thermal treatments. It has been observed that the martensitic transformation is associated with the variants of the product. Two orientations of the martensitic phase were observed as adjacent regions in quenched alloys. These orientations were forming in such a manner that they bore a common (111) plane and their b and c axes were interchanged. The slow cooled samples and those annealed at intermediate temperatures (650°C) showed (111) twinning in addition to the variants of the same transformation. The morphology of the (111) twinned product appeared as alternating platelets forming as adjacent regions. The samples that were aged at low temperatures (200°C) appeared to show internal twinning on (010) plane. The formation of these variants is considered in relation to the existing theories of the martensitic transformation. A possible mechanism of the shape memory phenomenon is also discussed.

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I. Introduction

In earlier reports (1)(2) on the martensitic transformation in Ti-Ni alloys of the near-equiatomic composition, it has been shown that there are at least six martensite or martensite-like structures in these alloys. Four out of these six are stacking modulated structures of the types 2H, 3R, 4H, and 4R and have orthorhombic unit cells. These martensites are formed on the close packed (111) plane of the CuAu-type basic structure. In certain orientations of the foil, it was observed that, two sets of reflections appeared simultaneously in our electron diffraction studies. These constituted the bulk of the specimen and were indexed on the basis of two monoclinic martensitic products $\beta'$ and $\beta''$. The $\beta'$ martensite in these alloys was reported to possess the lattice parameters

$$a = 2.9 \, \text{Å}, \quad b = 4.63 \, \text{Å}, \quad c = 4.11 \, \text{Å}, \quad \text{and} \quad \gamma = 96.7^\circ$$

within an experimental error of ±1%. The $\beta''$ martensite in the present investigation can also be indexed on the basis of a variant of the $\beta'$-$\beta''$ transformation. The only difference is that the observed reflections from the indexed $\beta''$ phase in electron diffraction studies do not match very well with the lattice parameters of the $\beta'$ phase either observed here or reported by other investigators(3)(4). There is always a discrepancy of about 1 to 2° in the angle between the (110) and (001) planes (Note: From the observed lattice parameters of the $\beta'$ phase, these reflections should be inclined at 90° to each other). This difference is very consistently observed through the investigation and it was not clear whether to treat this set of reflections as a slightly distorted variant of the same transformation or as a separate phase having a similar orientation relationship as the $\beta'$ phase has with the parent $\beta$ phase. In fact, that is what has led us to treat the other set of reflections as a separate phase initially. In the present report the other set of reflections will be treated as a variant of the same transformation, the reason for this interpretation will be clarified in later sections.

In the past, many attempts have been made to correlate the mechanical memory property of these alloys(5)(6). The result is not very conclusive, probably from the insufficient information of the structure of martensite as well as the variants of the transformation, twinning, etc., that generally arise in such transformations. To date no evidence of the twinning variant of the martensitic product in TiNi alloys is available. It is the purpose of the present investigation to report these crystallographic variants as observed under various thermal treatments. This report will also present the orientation relationship between the parent and the product martensitic phases. These may shed some light towards a better understanding of the peculiar mechanical memory property of TiNi alloys.

II. Experimental Procedure

The alloy preparation and fabrication technique and details of the electron microscopic observations are reported in an earlier paper(1) and hence will not be repeated here.

III. Experimental Results

The microstructure of quenched TiNi alloys of the near equiatomic composition consists of the alternat-

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* Department of Materials Science and Engineering Washington State University, Pullman, Washington, U.S.A.

(1) S. P. Gupta, K. Mukherjee and A. A. Johnson: To be published in Materials Science and Engineering.

(2) S. P. Gupta, K. Mukherjee and A. A. Johnson: To be published in Materials Science and Engineering.


(6) M. J. Marcinkowski, A. S. Sastri and D. Koskimaki: Phil. Mag., 18 (1968), 945.
Fig. 1(a) Bright field image showing twin related $\beta'$ martensite, 48.5% Ni alloy annealed at 635°C for a period of 35 days.

(b) The electron diffraction pattern obtained from the area of Fig. 1(a) showing (111) twinning. (101) type zone axis.

(c) The corresponding schematic interpretation of Fig. 1(b).

Fig. 2(a) Bright field image showing twin related $\beta'$ martensite, 45% Ni alloy annealed at 660°C for a period of one week.

(b) The corresponding electron diffraction pattern from area A of Fig. 2(a), (101) type zone axis.
is the presence of superlattice reflections which gave rise to additional reflections from a double diffraction effect. All other features including the twin plane and the direction of streaking are similar. The bright field image of the area from which the electron diffraction pattern of Fig. 2(b) was derived shows a similar alternating platelet characteristic which infers a twin relation, Fig. 2(a). This sample had many areas in which (111) twinning was apparent.

Electron diffraction patterns showing (111) twinning plane for the martensite were also recorded as shown in the diffraction pattern of Fig. 3(b) which represents a (110) type zone axis. All reflections that appear in this diffraction pattern are allowed except for those of the type (001) which can only occur by a double diffraction effect. This diffraction pattern was derived from the area labeled A in Fig. 3(a), which is a bright field image obtained from a 48% Ni alloy furnace cooled after annealing at 900°C. The alternating platelet morphology of the $\beta'$ and its twin was confirmed in some cases from the presence of straight thickness fringes lying parallel to the common interface. The electron diffraction patterns obtained from such regions showed no additional reflections from the parent bcc phase in contrast to the quenched samples which always showed these reflections. Some of the results on these will be described later. The thickness of the alternating regions of the martensite and its twin was not equal. These were found to vary from 1:1.5 to 1:3. The thickness ratio was further affected in the tilting experiments in the same region, often revealing a reversal of contrast.

In addition to the (111) twinning which was very frequently observed, (011) twinning was observed in some occasions. The electron diffraction pattern of Fig. 4(b) illustrates such a characteristic in a (011)
orientation of the foil. All reflections of this electron diffraction pattern are allowed by the structure factor of the 2H modulation on the CuAu type structure. The morphology was again found to be alternating platelet type as observed for the (111) twinning.

In order to study the effect of low temperature aging on the \(\beta'\) martensite and its variant, some of the alloys were aged at around 200°C after quenching from higher temperatures (<900°C). The aging treatment eliminated the variant of the \(\beta'\) martensite in some regions which was replaced by an internally twinned structure on the (010) planes, Figs. 5(a) and 5(b). The corresponding indexing for these figures is not shown here as these can be seen from Fig. 1(c) which is in the same orientation except for the twinning plane. The size of the primary martensite plate that is internally twinned was found to be increased after such a treatment as shown in the bright field images of Fig. 5(c). Each plate in this photograph shows internal striations. The diffraction pattern of Fig. 5(b) which is derived from these plates (Fig. 5(c)) clearly indicates two sets of reflections, one from each plate, which are twin related with the (010) \(\beta'\) plane being the twin plane of the monoclinic lattice. An approximate trace analysis has indicated that the (010) twinning plane coincides with the striations within the plates. The interface of these plates is found to be very wavy in nature in contrast to the (111) interface which was planar. The diffraction pattern of Fig. 5(b) further shows that there are strong streaking in directions perpendicular to the (010) plane. This direction will be inclined by 6.7° to the principal [010] direction of this phase. Electron diffraction patterns having different zone axis but showing (010) twinning were also
Fig. 6(a) Bright field image showing (010) twinning in a 48% Ni alloy aged at 225°C for a period of 3 weeks.
(b) The corresponding electron diffraction pattern, (101) type zone axis.

recorded as shown in Fig. 5(d). It is a (201) type zone axis of the martensitic phase, Fig. 5(e). The observed intensity of various reflections are very consistent with the calculated value for this structure. The internally twinned structure is very clearly revealed in the bright field image of Fig. 5(f), which is derived from a 45% Ni alloy. Other compositions also produced evidence of (010) twinning in these alloys. The alternate platelet morphology and internal striations within the platelets, however, were not so distinct as observed in the case of a 45%Ni alloy. An electron micrograph and the corresponding diffraction pattern revealing such a characteristic are shown in Fig. 6. On comparing the diffraction patterns of Figs. 5(b) and 6 it is apparent that they are identical. The direction of streaking and the morphology are again quite similar except for the striations which are less dense.

The electron diffraction patterns and the microstructural features that have been reported so far contained a twin related martensite. This, however, was not always the case. In several cases variants of the phase, typical of the quenching treatment, were found to be associated with the twin variant. The twinning plane was the same as in their respective annealing treatment i.e., the annealing at intermediate temperatures (650°C) produced (111) twinning whereas the low temperature treatment (200°C) generated (010) twinning. It is believed that the transformation to the twin variant is not completed in these regions. This is revealed in the electron diffraction pattern of Fig. 7 which also shows the area from which this pattern was derived. The common trace of the two planes is the (111) twinning-plane which coincides with the

Fig. 7(a)(b) Bright field image and the corresponding electron diffraction pattern showing orientation variants and the twinning variant simultaneously. The twinning variant reflections are arrowed, 48% Ni alloy aged for one week at 660°C. (101) type zone axis.
Fig. 8(a)(b) Electron diffraction pattern and its schematic showing (010) twinning and variant of the transformation, 45% Ni alloy aged for 3 weeks at 225°C. (101) zone axis.
(c) Bright field image of the area which produced the diffraction pattern of Fig. 8(a) (010) twin trace is parallel to the (111) interface of the variant.

(111) plane of the variant of the martensitic phase. The morphology is identical to the earlier reported morphology of the β' and its twin which forms as alternating platelets. The other type of transformation where the variant of the martensitic phase was retained along with the (010) twinning is shown in the electron diffraction pattern of Fig. 8. The primary martensite plates are in a twinned orientation, the twinning plane being the (111) plane. This produces reflections shown by the subscript A, Fig. 8(b). These plates are further twinned on a (010) plane shown in the figure by the subscript "t". The third set of reflections shown by the subscript "B" belong to the variant of the β' phase in a (110) orientation. From Figs. 8(a) and 8(b), it is seen that when the primary martensite plate is twinned on (111) plane, the (020) reflections will almost overlap the (11̅1) reflection. Thus fine striations within the plates due to internal twinning will lie almost parallel to the trace of the (11̅1) plane which is the common plane of the martensite and its variant. This is what is precisely observed in the microstructure of the area from which the electron diffraction pattern of Fig. 8(a) was derived, Fig. 8(c). This is also very consistent with those reported earlier.

Another very interesting feature that is observed in these alloys is the simultaneous formation of two

Fig. 9(a)(b) Electron diffraction pattern and its schematic showing two orientations of the martensite, (101) and (110) type sections. Reflections from the retained BCC phase can also be seen in a (111) orientation, 48% Ni alloy.
(c) Bright field image showing alternating platelet morphology of the two orientations. The (11̅1) plane forms as a common interface, 49.25% Ni alloy quenched from 900°C.
different orientations of the martensite. This is shown in the diffraction pattern of Fig. 9 along with its schematic interpretation. Two of the three sets of reflections that are observed here belong to the \( \beta' \) phase; one each from (101) and (110) orientations. The third set of reflections is indexed as the parent \( \beta \) phase in a (111) orientation. Reflections from the retained \( \beta \) phase were not observed when twin variant in the same orientation was observed. The diffraction pattern of Fig. 9 further suggests that some of the bcc reflections are slightly away from the exact position e.g., the (011) and (101) \( \beta \) are inclined at 56° instead of 60° suggesting a slight distortion of the parent phase during the martensitic transformation. The alternating platelet morphology from a different specimen in this particular orientation is shown in Fig. 9(c). The following approximate orientation relationship between the parent and the product phases:

\[
\begin{align*}
A &: (010)_B // (011)_P, [011]_B // [111]_P \\
B &: (001)_B // (011)_P, [110]_B // [111]_P
\end{align*}
\]

and those between the variants of the martensitic phase

\[
(1\bar{1}1)_{A1} // (1\bar{1}T)_B
\]

can be noted. The direction of streaking is inclined by

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**Fig. 10(a)(b)**  Electron diffraction pattern and its schematic showing two orientations of the martensite, (112) and (121) type sections.

(c) Bright field image that produced the diffraction pattern of Fig. 10(a), 48% Ni alloy.

(d)(e) and (f) Dark field photographs from (111), (111) and (101) reflections of Fig. 10(a).
approximately 5° to the (111) plane normal in contrast to the twinning case where it was parallel to the above plane normal. The microstructure in these cases indicated an alternating platelet type, the common interface of the two variants was found to be the (111) plane.

The electron diffraction pattern of Fig. 10 and the associated bright field and dark field electron micrographs further show the formation of two variants of the β' phase in a different orientation. Here (121) and (112) orientations are lying parallel to the electron beam. The morphology is again alternating platelet type as proved in the subsequent dark field photographs. In many occasions, only one set of reflections from the phase was observed. This was primarily due to limitations in electron diffraction of about 3 to 4° and not from an absence of the variant of this phase. Another orientation in which variants of the martensitic phase was observed is shown with the aid of the diffraction pattern of Fig. 11. The pattern suggests that the alternating platelets are in (101) and (121) orientations. The platelet morphology is accompanied by interfacial dislocations in such a case as shown in the bright field image of Fig. 11(b). In rare occasions these alternating platelets revealed the dislocation structure very clearly, Fig. 11(c). These were generally observed under tilting of the foil, the exact orientation, however, was difficult to determine because of an incomplete diffraction pattern under such conditions. It should be mentioned that dislocations at the interface of the martensite and its variants were very rarely observed in these alloys. It has been observed that variants of the same transformation whose b and c axes are interchanged were most common to appear. The combination of other variants are shown here to complete the other possibilities that were experimentally observed. The following table gives a summary of the martensite variants observed under a

![Fig. 11(a)(b)](image)

Electron diffraction pattern and its schematic showing two orientations of martensite, (101) and (121) sections, 49.25% Ni alloy quenched from 945°C.

![Fig. 11(c)](image)

(c) Bright field image that produced the electron diffraction pattern of Fig. 11(a). Dislocations can be seen at the interface.

![Fig. 11(d)](image)

(d) Bright field image showing the dislocation structure at the interface of two martensitic variants, 49.25% Ni alloy quenched from 900°C.
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IV. Discussion and Summary of Results

The orientation relationship between parent and the martensitic phase has been observed to be

$$\langle 001 \rangle_p // \langle 011 \rangle_s$$

$$\langle 110 \rangle_p // \langle 111 \rangle_s$$

within 2 to 3°. This orientation relationship is the same as those reported for the body centered cubic to orthorhombic transformation in Au–Cd\(^{(7)}\) alloys. By utilizing the respective lattice parameters, the planar orientation relationship between these phases is represented by stereographic projections of Fig. 12. The deviation between various planes of the bcc lattice and the corresponding planes of the monoclinic lattice is within reasonable limits as observed in the electron diffraction patterns of Figs. 3 and 9.

A direct calculation of the habit plane could not be attempted as can be realized from the complexities involved in such calculations where the product lattice is monoclinic. However, this has been attempted on the basis of the direct observation. In the present study based on at least 10 different diffraction patterns, strong streaking in a direction approximately $8 \pm 1/2$ away from (110) bcc towards the (011) bcc phase was observed in those samples where the martensitic phase was observed with its variant and a substantial amount of the bcc phase was retained. If it is assumed that such a strong streaking arises from the habit plane, as generally interpreted, then this will lie within a degree of (551) bcc plane. This type of analysis has been utilized by Ericksen et al.\(^{(8)}\) while studying the martensitic transformation in Ti–Cr alloys, where the (334) bcc plane is the habit plane. It should be pointed out that the (551) plane is inclined by about 5° from the (111) plane of the martensitic phase and does not correspond to any of the relevant planes in terms of twinning etc.

The martensitic transformation in TiNi alloys is observed to show three different twinning planes, i.e., (1\{1\}), (011), and (010). The first of these three planes, i.e., (1\{1\}) is the twinning generally observed in many nonferrous martensitic products where the starting structure is of the bcc type\(^{(9)(10)}\). The (1\{1\}) twinning in other alloy systems (AuCd, Cu–Al, etc.) has been interpreted as inhomogeneous transformation distortion. We assign the same interpretation to this twinning in the TiNi alloy and therefore it confirms with the crystallographic theories of the martensitic transformation after W–L–R\(^{(11)}\) and Bowles and Mackenzie\(^{(12)(13)(14)}\). The (1\{1\}) twinning belongs to the class A transformation in terms of the martensitic theories. In class B transformation, generally observed in Ti base alloys, the (011) plane of the orthorhombic lattice acts as a twinning plane and is generated from the (001) bcc plane. In the present investigation there was only one instance where (011) twinning was observed, Fig. 4. This does not give sufficient evidence to warrant a class B transformation in these alloys and thus can be regarded as accidental. The planes of reflection symmetry of a bcc lattice are the \{100\} and \{110\} planes. The (100), (110), (101), and (101) bcc planes correspond to four \{111\} planes of the martensite and the choice of one of these possibilities simply leads to a variant of the same transformation. The (1\{1\}) twinning observed in these alloys can be regarded as a variant of the (1\{1\}) twinning. The (010) twinning should not be observed when the martensitic

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(9) R. S. Toth and S. Sato: Acta Met., 16 (1968), 413.
(11) M. S. Wechsler, D. S. Lieberman and T. A. Read: Trans AIME, 195 (1953), 1803.
product has an orthorhombic lattice as would be the case in AuCd alloys. Because then the twinned crystal will be identical to the main structure and would not generate additional reflections from the twin. In the present study where a and b axes of the martensitic lattice are inclined at 96.7° instead of 90° to each other, the (010) twinning is feasible. The exact reason for such a transformation in terms of the crystallographic theories, however, is not understood.

The monoclinic martensite of the TiNi alloy is very similar to the orthorhombic product observed in AuCd alloys\(^{(15)}\). In both these alloy systems, the martensite is generated from a CsCl type lattice. Because of the cubic symmetry of the parent, the single contraction axis along which the distortion \(\eta_1\) occurs is equally probable along any of the three cubic directions of the parent. Since \(b\) and \(c\) of the orthorhombic lattice, which is generated from two \(\{011\}\) type bcc planes, can be interchanged, there are six equally probable Bain distortions as suggested by Lieberman\(^{(16)}\). Thus variants of the martensitic product would be expected to be found in adjacent regions of the crystal. It has been shown by Lieberman et al.\(^{(16)}\) that vectors in adjacent regions will be affected oppositely under such transformations. To satisfy the crystallographic theories of the martensitic transformation, an invariant habit plane can be generated if adjacent regions of the crystal form as volume fraction \(X\) and \((1-X)\) thus minimizing the strain energy associated with fitting the two structures at the interface during the transformation. A cooperative total rotation \(\phi\) will be required to form a common interface. From energetic consideration, however, Lieberman et al.\(^{(16)}\) have shown that formation of a twinned structure will be favored over a variant of the same transformation. Such twins (III) were found to form in TiNi alloys annealed at intermediate temperatures. The formation of the variants of the transformation, although theoretically possible, can be attributed to be associated either with the quenching stresses or the substitutional defect structure. The earlier misinterpretation\(^{(2)}\) of the other set of reflection as a separate martensitic phase will be clarified here. In those cases where variants of the martensitic transformation product were observed, it was found that (1\(\bar{T}\)) plane formed as a common interface. As mentioned above, a rotation will be required to fit the two variants at the (1\(\bar{T}\)) interface and it is presumed that during this rotation a slight distortion occurs in one of the variants leading to the observed diffraction patterns where (001) and (110) reflections are inclined at approximately 91.5° instead of 90°.

From the results of the present investigation, although limited only to the structural characteristics of the martensite and its variant, some points can be made as to the possible mechanism responsible for the shape memory effect observed in TiNi alloys. Two types of transformations will be mainly considered, i.e., (a) when the martensite occurs along with its variant and (b) when the martensite forms as a twin (1\(\bar{T}\)) in adjacent regions.

In the first case, the total transformation distortion is inhomogeneous by virtue of a variant in adjacent regions and that the (1\(\bar{T}\)) plane is a coherent interface similar to the one observed when twinning is the product of an inhomogeneous transformation distortion. In a completely transformed material having two variants of the martensitic phase, the plastic deformation will cause the growth or creation of the favourably oriented variant and the shrinkage or disappearance of the unfavourably oriented variant. The deformation will be realized by the movement of the coherent (1\(\bar{T}\)) interface.

In samples which are partly transformed to the martensitic phase, as typical of the quenched samples, the deformation, upon the application of the stress, will be realized by the transformation of the parent bcc phase to the favourably oriented variant of the martensitic phase in addition to the process described above. In subsequent deformation-heating-deformation cycles more of the retained parent phase will transform to martensite thus increasing the total recovery of the shape memory property. In this case it is essential that the slip does not take place during the deformation process, otherwise the shape memory will not be recovered.

The shape memory phenomenon in those alloys which possessed a (1\(\bar{T}\)) twinned martensite (case B) can be explained in terms of the movement of the coherent twin interface during deformation as observed in the Au–Cd alloys.

The present mechanism explains that, upon deformation, favourable variants of the martensite will grow at the expense of the other. On reversal of the stress (compressive if originally tensile and vice versa), the variant that was unfavourable will grow. This will produce two types of texture in these alloys if specimens were given tensile and compressive stresses. This is what was observed by de Lange and Zijderveld\(^{(5)}\) in their observation on these alloys. The phenomenon of mechanical memory, however, was explained in terms of the transformation (bcc to martensite) only. By contrast, the present mechanism can also explain the memory effect in alloys that are fully transformed. This point was also made by Otsuka et al.\(^{(17)}\) in their explanation of the shape memory which they attributed only on the basis of the twinned martensitic structure. The twinned structure is not the only structure observed here. Moreover, if the mechanical memory effect is explained only in terms of the formation of twinned martensite from one of the variants in quenched alloys, then one would not detect different textures observed by de Lange et al.\(^{(5)}\). In addition, this mechanism although similar to the one proposed and observed for AuCd and Cu–Al–Ni\(^{(18)}\)

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alloys can also explain the increased recovery of the shape memory in subsequent cycles of deformation-heating-deformation as generally reported for TiNi alloys.

This report summarizes the structural transformation in near-equatomic Ti-Ni alloys under varying conditions of heat treatment. The role of the variant of the martensitic product is described in terms of the general crystallographic theories and has been attributed to be responsible for the shape memory phenomenon. However, the formation of dislocations in few instances and the (010) fine internal twin and the role they play remain unexplained.